

05-1-00

A

Practitioner's Docket No.

Refrac-3

PATENT

Preliminary Classification:

Proposed Class:

Subclass:

NOTE: "All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P. § 601, 7th ed.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application

Assistant Commissioner for Patents

Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): Becker, R.C. and Bunker, S.L.

WARNING: 37 C.F.R. § 1.41(a)(1) points out:

"(a) A patent is applied for in the name or names of the actual inventor or inventors.

"(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(f) is filed supplying or changing the name or names of the inventor or inventors."

For (title):

Method for Depositing Boron-Rich Coatings

CERTIFICATION UNDER 37 C.F.R. § 1.10*(Express Mail label number is **mandatory**.)

(Express Mail certification is optional.)

I hereby certify that this New Application Transmittal and the documents referred to as attached therein are being deposited with the United States Postal Service on this date 28 Apr 2000, in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EE 9313523000, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

D.N. Halgrett
(type or print name of person mailing paper)

[Signature]
Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. § 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

***WARNING:** Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. § 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

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04/28/00
JC806 U.S. PTO

JC678 U.S. PTO
09/560518
04/28/00

05560518 042800

1. Type of Application

This new application is for a(n)

(check one applicable item below)

☒ Original (nonprovisional)

☐ Design

☐ Plant

WARNING: Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. § 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.

WARNING: Do not use this transmittal for the filing of a provisional application.

NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

☐ Divisional.

☐ Continuation.

☐ Continuation-in-part (C-I-P).

2. Benefit of Prior U.S. Application(s) (35 U.S.C. §§ 119(e), 120, or 121)

NOTE: A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. § 112. Each prior application must also be:

(i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or

(ii) Complete as set forth in § 1.51(b); or

(iii) Entitled to a filing date as set forth in § 1.53(b) or § 1.53(d) and include the basic filing fee set forth in § 1.16; or

(iv) Entitled to a filing date as set forth in § 1.53(b) and have paid therein the processing and retention fee set forth in § 1.21(l) within the time period set forth in § 1.53(f).

37 C.F.R. § 1.78(a)(1).

NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

WARNING: If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. §§ 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. §§ 120, 121 or 365(c). (35 U.S.C. § 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. §§ 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.

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Based on Provisional Applic. #60/150,205
filed 08/21/1999 from which the
Present Application springs

WARNING: When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application **must** be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).

- ☐ The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

3. Papers Enclosed

- A. Required for filing date under 37 C.F.R. § 1.53(b) (Regular) or 37 C.F.R. § 1.153 (Design) Application

25 Pages of specification

4 Pages of claims

2 Sheets of drawing

WARNING: **DO NOT** submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 C.F.R. § 1.84, see Notice of March 9, 1988 (1990 O.G. 57-62).

NOTE: "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page . . ." 37 C.F.R. § 1.84(c).

(complete the following, if applicable)

- ☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. § 1.84(b).
- ☐ formal
- ☐ informal

B. Other Papers Enclosed

___ Pages of declaration and power of attorney

1 Pages of abstract

___ Other

4. Additional papers enclosed

- ☐ Amendment to claims
- ☐ Cancel in this applications claims _____ before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)
- ☐ Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)
- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement (37 C.F.R. § 1.98)
- ☐ Form PTO-1449 (PTO/SB/08A and 08B)
- ☐ Citations

- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other

5. Declaration or oath (including power of attorney)

NOTE: A newly executed declaration is not required in a continuation or divisional application provided that the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47, then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. §§ 1.63(d)(1)–(3).

NOTE: A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name including family name and at least one given name, without abbreviation together with any other given name or initial, and the residence, post office address and country or citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. § 1.63(a)(1)–(4).

NOTE: "The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.62, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(f) is filed supplying or changing the name or names of the inventor or inventors." 37 C.F.R. § 1.41(a)(1).

- ☐ Enclosed

Executed by

(check all applicable boxes)

- ☐ inventor(s).
- ☐ legal representative of inventor(s).
37 C.F.R. §§ 1.42 or 1.43.
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
 - ☐ This is the petition required by 37 C.F.R. § 1.47 and the statement required by 37 C.F.R. § 1.47 is also attached. See item 13 below for fee.

- ☒ Not Enclosed.

NOTE: Where the filing is a completion in the U.S. of an International Application or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.

- ☐ Application is made by a person authorized under 37 C.F.R. § 1.41(c) on behalf of all the above named inventor(s).

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(The declaration or oath, along with the surcharge required by 37 C.F.R. § 1.16(e) can be filed subsequently).

- ☐ Showing that the filing is authorized.
(not required unless called into question. 37 C.F.R. § 1.41(d))

6. Inventorship Statement

WARNING: If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.

The inventorship for all the claims in this application are:

☒ The same.

or

- ☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,
- ☐ is submitted.
- ☐ will be submitted.

7. Language

NOTE: An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of \$130.00 required by 37 C.F.R. § 1.17(k) is required to be filed with the application, or within such time as may be set by the Office. 37 C.F.R. § 1.52(d).

- ☒ English
- ☐ Non-English
- ☐ The attached translation includes a statement that the translation is accurate. 37 C.F.R. § 1.52(d).

8. Assignment

- ☒ An assignment of the invention to IBADEX LLC
- ☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.
- ☒ will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

WARNING: A newly executed "CERTIFICATE UNDER 37 C.F.R. § 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.

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003240 3159560

9. Certified Copy

Certified copy(ies) of application(s)

Country	Appln. No.	Filed
Country	Appln. No.	Filed
Country	Appln. No.	Filed

from which priority is claimed

- ☐ is (are) attached.
☐ will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 C.F.R. § 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. § 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. Fee Calculation (37 C.F.R. § 1.16)

- A. ☒ Regular application

CLAIMS AS FILED			
Number filed	Number Extra	Rate	Basic Fee 37 C.F.R. § 1.16(a) \$690.00
Total			
Claims (37 C.F.R. § 1.16(c))	20 - 20 = —	× \$ 18.00	—
Independent Claims (37 C.F.R. § 1.16(b))	2 - 3 = —	× \$ 78.00	—
Multiple dependent claim(s), if any (37 C.F.R. § 1.16(d))		+ \$260.00	

- ☐ Amendment cancelling extra claims is enclosed.
☐ Amendment deleting multiple-dependencies is enclosed.
☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 C.F.R. § 1.16(d).

Filing Fee Calculation

\$ 660.00

- B. ☐ Design application
(\$310.00—37 C.F.R. § 1.16(f))

Filing Fee Calculation

\$ _____

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\$_____

13. Fee Payment Being Made at This Time

☒ Not Enclosed

☒ No filing fee is to be paid at this time.

(This and the surcharge required by 37 C.F.R. § 1.16(e) can be paid subsequently.)

☐ Enclosed

☐ Filing fee

\$ _____

☐ Recording assignment

(\$40.00; 37 C.F.R. § 1.21(h))

(See attached "COVER SHEET FOR
ASSIGNMENT ACCOMPANYING NEW
APPLICATION".)

\$ _____

☐ Petition fee for filing by other than all the
inventors or person on behalf of the inventor
where inventor refused to sign or cannot be
reached

(\$130.00; 37 C.F.R. §§ 1.47 and 1.17(i))

\$ _____

☐ For processing an application with a
specification in

a non-English language

(\$130.00; 37 C.F.R. §§ 1.52(d) and 1.17(k))

\$ _____

☐ Processing and retention fee

(\$130.00; 37 C.F.R. §§ 1.53(d) and 1.21(l))

\$ _____

☐ Fee for international-type search report

(\$40.00; 37 C.F.R. § 1.21(e))

\$ _____

NOTE: 37 C.F.R. § 1.21(l) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 C.F.R. § 1.53(f) and this, as well as the changes to 37 C.F.R. §§ 1.53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1.21(l) must be paid, within 1 year from notification under § 53(f).

Total fees enclosed

\$ _____

14. Method of Payment of Fees

☐ Check in the amount of \$ _____

☐ Charge Account No. _____ in the amount of
\$ _____

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 C.F.R. § 1.22(b).

(New Application Transmittal [4-1]—page 8 of 11)

15. Authorization to Charge Additional Fees

WARNING: If no fees are to be paid on filing, the following items should not be completed.

WARNING: Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

- ☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. _____:

- ☐ 37 C.F.R. § 1.16(a), (f) or (g) (filing fees)
☐ 37 C.F.R. § 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

- ☐ 37 C.F.R. § 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)
☐ 37 C.F.R. § 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a)).
☐ 37 C.F.R. § 1.17 (application processing fees)

NOTE: “. . . A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission.” 37 C.F.R. § 1.136(a)(3).

- ☐ 37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. § 1.28(b) requires “Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . the issue fee. . . .” From the wording of 37 C.F.R. § 1.28(b), (a) notification of change of status must be made even if the fee is paid as “other than a small entity” and (b) no notification is required if the change is to another small entity.

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0956518 04300

16. Instructions as to Overpayment

NOTE: "... Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).

☐ Credit Account No. _____

☒ Refund

002240" 27509560

Reg. No. 27056

Tel. No. 17526-8000

Customer No.



SIGNATURE OF PRACTITIONER

(type or print name of attorney)

P.O. Address

Donald N. Halgren

35 Central St

Manchester NH 03104

(New Application Transmittal [4-1]—page 10 of 11)

☒ **Incorporation by reference of added pages**

(check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

- ☒ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added 5

- ☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added _____

- ☐ Plus added pages deleting names of inventor(s) named in prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added _____

- ☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added _____

☐ **Statement Where No Further Pages Added**

(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)

- ☐ This transmittal ends with this page.

ADDED PAGES FOR APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED

NOTE: See 37 C.F.R. § 1.78.

17. Relate Back

WARNING: If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. §§ 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. §§ 120, 121 or 365(c). (35 U.S.C. § 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. §§ 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.

(complete the following, if applicable)

☒ Amend the specification by inserting, before the first line, the following sentence:

A. 35 U.S.C. § 119(e)

NOTE: "Any nonprovisional application claiming the benefit of one or more prior filed copending provisional applications must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior provisional application, identifying it as a provisional application, and including the provisional application number (consisting of series code and serial number)." 37 C.F.R. § 1.78(a)(4).

☒ "This application claims the benefit of U.S. Provisional Application(s) No(s).:

APPLICATION NO(S).:

60, 150, 205

FILING DATE

08/21/99

B. 35 U.S.C. §§ 120, 121 and 365(c)

NOTE: "Except for a continued prosecution application filed under § 1.53(d), any nonprovisional application claiming the benefit of one or more prior filed copending nonprovisional applications or international applications designating the United States of America must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior application, identifying it by application number (consisting of the series code and serial number) or international application number and international filing date and indicating the relationship of the applications. . . . Cross-references to other related applications may be made when appropriate." (See § 1.14(a)). 37 C.F.R. § 1.78(a)(2).

☒ "This application is a

☐ continuation

☒ continuation-in-part

☐ divisional

of copending application(s)

☐ application number 0 / _____ filed on _____"

☐ International Application _____ filed on _____

_____ and which designated the U.S."

NOTE: The proper reference to a prior filed PCT application that entered the U.S. national phase is the U.S. serial number and the filing date of the PCT application that designated the U.S.

NOTE: (1) Where the application being transmitted adds subject matter to the International Application, then the filing can be as a continuation-in-part or (2) if it is desired to do so for other reasons then the filing can be as a continuation.

NOTE: The deadline for entering the national phase in the U.S. for an international application was clarified in the Notice of April 28, 1987 (1079 O.G. 32 to 46) as follows:

"The Patent and Trademark Office considers the International application to be pending until the 22nd month from the priority date if the United States has been designated and no Demand for International Preliminary Examination has been filed prior to the expiration of the 19th month from the priority date and until the 32nd month from the priority date if a Demand for International Preliminary Examination which elected the United States of America has been filed prior to the expiration of the 19th month from the priority date, provided that a copy of the international application has been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively. If a copy of the international application has not been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively, the international application becomes abandoned as to the United States 20 or 30 months from the priority date respectively. These periods have been placed in the rules as paragraph (h) of § 1.494 and paragraph (i) of § 1.495. A continuing application under 35 U.S.C. 365(c) and 120 may be filed anytime during the pendency of the international application."

☐ "The nonprovisional application designated above, namely application

_____ / _____, filed _____, claims the benefit of

U.S. Provisional Application(s) No(s):

APPLICATION NO(S):

FILING DATE

_____ / _____

_____ "

_____ / _____

_____ "

_____ / _____

_____ "

☐ Where more than one reference is made above, please combine all references into one sentence.

18. Relate Back—35 U.S.C. § 119 Priority Claim for Prior Application

The prior U.S. application(s), including any prior International Application designating the U.S., identified above in item 17B, in turn itself claim(s) foreign priority(ies) as follows:

Country	Appln. no.	Filed on
---------	------------	----------

The certified copy(ies) has (have)

- ☐ been filed on _____, in prior application 0 / _____, which was filed on _____.
- ☐ is (are) attached.

WARNING: The certified copy of the priority application that may have been communicated to the PTO by the International Bureau may **not** be relied on without any need to file a certified copy of the priority application in the **continuing application**. This is so because the certified copy of the priority application communicated by the International Bureau is placed in a folder and is not assigned a U.S. serial number unless the national stage is entered. Such folders are disposed of if the national stage is not entered. Therefore, such certified copies may not be available if needed later in the prosecution of a continuing application. An alternative would be to physically remove the priority documents from the folders and transfer them to the continuing application. The resources required to request transfer, retrieve the folders, make suitable record notations, transfer the certified copies, enter and make a record of such copies in the Continuing Application are substantial. Accordingly, the priority documents in folders of international applications that have not entered the national stage may not be relied on. Notice of April 28, 1987 (1079 O.G. 32 to 46).

19. Maintenance of Copendency of Prior Application

NOTE: The PTO finds it useful if a copy of the petition filed in the prior application extending the term for response is filed with the papers constituting the filing of the continuation application. Notice of November 5, 1985 (1060 O.G. 27).

A. ☐ Extension of time in prior application

(This item **must** be completed and the papers filed in the **prior application**, if the period set in the prior application has run.)

- ☐ A petition, fee and response extends the term in the pending **prior application** until _____.
- ☐ A **copy** of the petition filed in prior application is attached.

B. ☐ Conditional Petition for Extension of Time in Prior Application

(complete this item, if previous item not applicable)

- ☐ A conditional petition for extension of time is being filed in the pending **prior application**.
- ☐ A **copy** of the conditional petition filed in the prior application is attached.

00560518-042800

20. Further Inventorship Statement Where Benefit of Prior Application(s) Claimed

(complete applicable item (a), (b) and/or (c) below)

- (a) ☐ This application discloses and claims only subject matter disclosed in the prior application whose particulars are set out above and the inventor(s) in this application are
- ☐ the same.
 - ☐ less than those named in the prior application. It is requested that the following inventor(s) identified for the prior application be deleted:

(type name(s) of inventor(s) to be deleted)

- (b) ☒ This application discloses and claims additional disclosure by ~~amendment~~ *new application* and a new declaration or oath is being filed. With respect to the prior application, the inventor(s) in this application are

☐ the same.

☒ the following additional inventor(s) have been added:

S. L. BUNKER

(type name(s) of inventor(s) to be added)

- (c) The inventorship for all the claims in this application are
- ☒ the same.
 - ☐ not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made
 - ☐ is submitted.
 - ☐ will be submitted.

21. Abandonment of Prior Application (if applicable)

- ☐ Please abandon the prior application at a time while the prior application is pending, or when the petition for extension of time or to revive in that application is granted, and when this application is granted a filing date, so as to make this application copending with said prior application.

NOTE: According to the Notice of May 13, 1983 (103, TMOG 6-7), the filing of a continuation or continuation-in-part application is a proper response with respect to a petition for extension of time or a petition to revive and should include the express abandonment of the prior application conditioned upon the granting of the petition and the granting of a filing date to the continuing application.

22. Petition for Suspension of Prosecution for the Time Necessary to File an Amendment

WARNING: "The claims of a new application may be finally rejected in the first Office action in those situations where (A) the new application is a continuing application of, or a substitute for, an earlier application, and (B) all the claims of the new application (1) are drawn to the same invention claimed in the earlier application, and (2) would have been properly finally rejected on the grounds of art of record in the next Office action if they had been entered in the earlier application." M.P.E.P., § 706.07(b), 7th ed.

NOTE: Where it is possible that the claims on file will give rise to a first action final for this continuation application and for some reason an amendment cannot be filed promptly (e.g., experimental data is being gathered) it may be desirable to file a petition for suspension of prosecution for the time necessary.

(check the next item, if applicable)

- ☐ There is provided herewith a Petition To Suspend Prosecution for the Time Necessary to File An Amendment (New Application Filed Concurrently)

23. Small Entity (37 C.F.R. § 1.28(a))

- ☐ Applicant has established small entity status by the filing of a statement in parent application /_____ on _____.
- ☐ A copy of the statement previously filed is included.

WARNING: See 37 C.F.R. § 1.28(a).

WARNING: "Small entity status must not be established when the person or persons signing the . . . statement can *unequivocally* make the required self-certification." M.P.E.P., § 509.03, 7th ed. (emphasis added).

24. NOTIFICATION IN PARENT APPLICATION OF THIS FILING

- ☐ A notification of the filing of this (check one of the following)
- ☐ continuation
 - ☐ continuation-in-part
 - ☐ divisional

is being filed in the parent application, from which this application claims priority under 35 U.S.C. § 120.

(Added Pages for Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed
[4-1.1]—page 5 of 5)

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**APPLICATION FOR U.S. PATENT IN THE
UNITED STATES PATENT AND TRADEMARK OFFICE**

Title: METHOD FOR DEPOSITING BORON-RICH COATINGS

Inventors: **Richard C. Becker**, Ipswich, Massachusetts
Stephen L. Bunker, Wakefield, Massachusetts

Assignee: **IBADEX LLC.**
Danvers, Mass.

FIELD OF INVENTION

The present invention relates to a method for producing boron-rich coatings for a variety of uses related to surface protection, sputter targets, electrically conductive layers, semiconductor compatibility, neutron absorption, high temperature bonding, and reactive chemistry.

BACKGROUND OF INVENTION

Elemental boron is a well-known hard, covalent material. It also possesses considerable chemical resistance and is suitable for high temperatures in a vacuum or reducing atmosphere. It is known to impart considerable wear resistance to tooling materials if the boron can be added in sufficient quantity or coated on the workpieces. Unfortunately, elemental boron is difficult to deposit at a high rate by most commonly used deposition techniques, such as flame spray, plasma spray, or cathodic arc, because as a covalent material, it does not readily conduct electricity (resistivity $\sim 10^{14}$ microhm-cm).

Many boride compounds do conduct electricity very well. For example, metal boride compounds, such as TiB_2 , VB_2 , CrB_2 , and LaB_6 have electrical resistivity in the range of 5 to 20 microhm-cm. However, these common boron compounds typically contain boron at a concentration only between 50 and 86 atomic %, and their use in a deposition process, such as plasma spray, would result in a coating containing a high concentration of the metal (14 to 50 atomic percent). It is possible to avoid the electrical conductivity problem by making use of the unusual properties of a novel class of metal boride compounds which typically consist of a

single atom of a metal together with a large number of atoms of boron. There exist two major classes of such boron-rich borides, one based on 12 atoms of boron (92.3 atomic % boron) and the other based on 66⁺ atoms of boron (98.5⁺ atomic % boron). Examples include yttrium-12 boride (YB₁₂) and yttrium-66 boride (YB₆₆). The members of these classes of borides are usually electrically conductive yet substantially consist solely of boron. Examples of reported electrical conductivities exist for some borides with an atomic ratio of 12. The values are typically in the range of 10 to 25 microhm-cm. It is possible that other borides with even higher boron-to-metal ratios exist. For example, YbB₁₀₀ and YB₁₂₄₋₁₂₈ have been reported.

Within these classes, the vaporization properties of the metal component diverge into two groups, those in which the metal evaporates prior to the evaporation of the boron and those in which the boron evaporates prior to the metal component. If the former group is utilized in a high temperature deposition system, the boride feedstock may gradually become surface depleted in the metal component which was providing the electrical conductivity. If the deposition process is dependent on the conductivity, it may be gradually halted as the feedstock presents a surface of pure boron. If the latter group is used as a source for deposition of boron coatings, the resultant boron coating can be substantially pure and free of metal, but not necessarily conductive. Members of each group may be useful depending on the method of deposition and intended application.

Only a limited number of elements exist which have known compounds in which the boron-to-element atomic ratio is greater than or equal to 12. Compounds of the form MB₁₂ where M represents the element include, but are not necessarily limited to, Al, Dy, Er, Ho, Li, Lu, Mg, Np, Pu, S, Sc, Tb, Th, Tm, U, Y, Yb, and Zr. Compounds of the form MB₆₆ where M

represents the element include, but are not necessarily limited to, Dy, Er, Eu, Gd, Ho, Lu, Np, Pa, Pu, Sm, Tb, Th, Tm, Y, and Yb. All of these latter elements are only in group 3A of the periodic table, which includes the rare earths, the lanthanides and the actinides. There have also been reported three other compounds with unusual boron-to-element atomic ratios, $B_{25}N$, NaB_{15} , NaB_{16} , and YbB_{100} . While most elements of the periodic table are known to make borides, only these elements produce highly boron-rich borides. There is also considerable overlap between the boride lists for 12 and 66 boron atoms. There are also a few examples of MB_{12} in group 1A, group 2A, group 3A, group 3B, group 5A and group 6A of the periodic table. The only reported example in groups 4B, 5B, or 6B is ZrB_{12} .

The use of group designations used here is based on common American usage. The earlier nomenclature would be group 1B instead of 1A for the first column of the periodic table. The column containing yttrium and the rare earth elements is now 3B but used to be 3A. The IUPAC recommends that this column be designated 3, but this is not yet universally accepted.

Examples of the group in which the boron evaporates at a lower temperature compared to the companion element include the borides of yttrium, gadolinium, terbium, holmium, erbium, thulium, and lutetium.

In addition to the known examples of boron-rich boride compounds, it is also possible to dope boron with small amounts of elements that can affect the electrical conductivity. Doping is the dissolution of the element in the boron crystal, and unlike compound formation, does not require a specific stoichiometric ratio between the element and the boron. This is an alternative method for producing an electrically conducting boron material which consists substantially of the element boron. An impure sample of a boron-rich boride in which the stoichiometric ratio of

the elements is somewhat different from that of a known compound may consist of a mixture of a known compound and doped boron material.

The known applications for inexpensive, easily deposited thick boron coatings are numerous. The general applications include, but are not limited to, those stated in the following list.

- 1) Electrically conducting coatings on electrical insulators and ceramics.

Using the method of plasma spray, boron-rich borides can be deposited onto a wide variety of ceramics and insulators including BN, Al_2O_3 , aerogel, ZrO_2 , quartz, and porcelain. Adhesion of borides to these materials, as well as to most metals, carbon, carbides, and nitrides is particularly strong. No substrate material has been encountered in which the plasma sprayed yttrium boride did not stick tightly to the surface, as long as the substrate is not thermally damaged by the deposition process.

- 2) Interior surfaces of semiconductor fabrication machines to minimize evolution of impurities.

Semiconductor wafers are particularly sensitive to impurity particles, such as metal dusts, that are deposited on wafers during a vacuum fabrication process. In order to avoid this phenomenon many semiconductor fabrication machines are now coated with silicon (not an impurity) on their interiors. The silicon is expensive to deposit over large areas and does not conduct electricity well, a problem leading to static charging of surfaces in processing equipment that employs charged particles. A thick conductive boron coating would avoid this problem, since boron is a natural dopant for silicon.

- 3) Boron-coated refractory hot filaments, such as tungsten, tantalum, or rhenium, to enhance electron output and minimize emission of metal vapor in high purity processing situations. See for example, US patent 3,631,291 by Louis J Favreau which utilizes a conductive coating of LaB_6 , which patent is incorporated herein by reference.

In some processing applications, particularly those for semiconductors, surface contamination from tungsten or tantalum impurities emitted from a nearby heated filament due to evaporation or sputtering is undesirable. A conductive boron-rich boride can be coated on such filaments using a method such as plasma spray. The resultant boron-rich coating readily emits electrons and substantially only boron vapor if the coating boride is selected from the group in which boron evaporates more readily than the metal. Since the coating is producing the electron emission, it is not necessary for the hot filament substrate to be a good electron emitting material. Other refractory materials, such as carbon, carbides, or nitrides, could be employed.

Coating technologies, such as plasma spray, can also produce free-standing filaments and heating elements without the requirement of a permanently attached substrate. The coating is built up into a mold, and when sufficient thickness is obtained, a mold release allows the removal of an independent, free-standing structure. This method permits the fabrication of a substantially pure boron filament without any contaminating substrate material.

- 4) Chemically resistant surface coating on containers.

Borides are well known to be highly resistant to many forms of chemical attack, particularly those due to high temperature molten metals, as long as a vacuum or reducing environment is maintained. Such chemically resistant surface coatings can be fabricated using a variety of well-known deposition techniques, such as salt bath, powder coating, chemical vapor

deposition, and evaporation. See, for example, US patent 4,536,224 by Beyer et al. for salt bath, US patent 5,441,762 by Paul E. Gray et al. for coating with boride powder combined with chemical vapor deposition, US patent 3,985,917 by Val J. Krukoni for chemical vapor deposition, and JP 10,068,069A by Satoru et al. for evaporation, each of which patents are each incorporated herein by reference. Electrically conductive boron-rich boride permits the use of a much broader selection of deposition methods which can be less expensive or more suitable for large area surface coating of such reaction crucibles and related apparatus.

Similar to the application example of refractory hot filaments, it is also possible to make a free-standing container of substantially pure boron by plasma spray coating a mold or mandril and subsequently separating the thick coating from the mold or mandril substrate.

Satoru et al. describe electric arc evaporative coating of borides in which the metal component of the boride is selected solely from Groups 4B, 5B, and 6B of the periodic table. Satoru et al. do not teach the advantages of selecting the ultra-high atomic percent borides that are found solely in Group 3B together with the rare earth elements for their application.

- 5) Wear and corrosion resistant coatings for tooling. See for example, US patent 4,192,983 by Alfred J. Paoletti, incorporated herein by reference.

Boride coatings are known for their extreme hardness. Coatings can be applied to tooling by any of several techniques, such as plasma spray, and as stated in example 1) above, adhesion is sufficient to permit grinding and polishing into shape if required. It has also been demonstrated that in the presence of a diffusable layer of boron-rich boride, adhesion of materials as dissimilar as tantalum and graphite may be promoted. This property is of great significance for bonding tools to toolstocks and general refractory bonding technology.

Similar to the application example of refractory hot filaments, it is also possible to make a free-standing wear and corrosion resistant solid structure of substantially pure boron by plasma spray coating a mold or mandril and subsequently separating the thick coating from the mold or mandril substrate.

- 6) Addition of boron atoms or ions at or near the surface of a workpiece for hardening and wear resistance, commonly referred to as boridizing.

Boridizing (or boronizing) is a process of diffusing boron atoms into surfaces in order to increase hardness without substantially altering the shape of the substrate. Usually this is accomplished at high temperature with the source of boron atoms provided by a powder packed in close proximity to the surface to be treated. See for example, US patent 4,011,107 by William J. Hayes, incorporated herein by reference. It is most commonly used with cutting tools. Other methods can be utilized to bring the boron atoms to the surface of the workpiece to be treated, including both vapor phase as well as ion phase. For example, a cathodic arc can transmit both coating and ions or if a mass filter is employed, it can transmit solely boron ions to the surface of the workpiece, where they are subsequently diffused into the volume thermally.

- 7) Thick coatings of neutron absorbing boron-10 isotope for use as a neutron shield or as a source of alpha particles produced in the absorption process.

Boron-10 is a well known isotope used for neutron absorption because of its high cross section. Coatings of boron, with or without isotopic enrichment of boron-10, can be applied to any substrate material compatible with nuclear reactors, fusion reactors, containment devices, or weapons, for use as a neutron shield. If plasma spray is employed, the boron coating can be made extremely thick in order to increase the effectiveness of the neutron absorption. It is also

possible to combine a well-known neutron absorbing element with boron in a suitable boride. See for example, US patent 5,273,709 by Danny C. Halverson et al., which is based on Gd combined with B₄C. Halverson et al. do not teach the advantages of selecting the ultra-high atomic percent borides that are found solely in Group 3B together with the rare earth elements for their application. These patents are also incorporated herein by reference.

- 8) Source for emission of clusters of boron atoms useful in space propulsion thrusters or ion sources.

Ion thrusters are currently used in space propulsion. Boron₁₂ ion clusters are the most common cluster species in the generated plasma. It has approximately the same mass as xenon, which is the heaviest noble gas available, and provides the greatest thrust. Being an electrically conductive solid state material, storage problems are eliminated, and potential energy per stored unit volume ratios increase significantly. Proper design engineering has demonstrated that after stable ignition has been established, the carrier gas may be eliminated and a self-sustaining discharge maintained.

- 9) Surface and/or bulk modification of metals, ceramics, and matrix materials.

The generated boron vapor may be introduced during fabrication, processing, and/or post-processing to modify properties of resultant materials. For example vapor or vaporizable material may be introduced into molten steel or other material at some state during the production process for purposes of altering hardness, chemical resistance, electrical properties, temperature resistance, etc. Boron is currently used in many of these areas. The novel properties of these boron-rich materials offer many valuable possibilities.

10) Protective coatings for fibers:

A common application is to coat the reinforcement fibers of composite materials with a boride compound in order to chemically protect the fiber from the corrosive molten binder material. See for example US patent 5,354,615 by Tenhover et al., incorporated herein by reference. Tenhover teaches the use of boride coatings of Y, Sc, Gd, Tb, Dy, Ho, and Er of the chemical form R_xB_{1-x} , where x is from about 0.05 to about 0.66. This range of x is equivalent to a boron-to-metal atomic ratio of 19 to 0.5. Tenhover et al. do not teach the advantages of ultra-high boron-to metal atomic ratios in excess of 19, which produce a more boron-like coating than is possible with lower ratios.

11) Erosion-resistant coating

Boron and boride coatings are usually extremely hard. They have demonstrated usefulness for reducing the surface erosion caused by macro-particle bombardment. See for example, US Patent # JP10148102A by Ikeda Kazuaki and Fujiwara Toshihiro, "Turbine Nozzle and Boride Covering Method Therefor", 1998, incorporated herein by reference. Examples of applications include compressor and turbine blades, steam generator components, and slurry-handling devices.

Boron or borides have been successfully coated onto substrates by a variety of well known methods. The most commonly described coating techniques are thermally induced evaporation of the element or of various borides, thermal diffusion of boron atoms into a surface, sputtering of any of the common electrically conductive borides with a boron-to-metal ratio less than 12, chemical vapor deposition, and molten salt bath. Other techniques described involve a

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mixture of these techniques, such as the cementing of boron or boride powder to a surface using a chemical binder combined with either chemical vapor deposition or thermal diffusion.

While these coating methods are compatible with the deposition of boron coatings, there exist a number of other commonly employed industrial coating techniques which offer various advantages in coating rate, ultimate coating thickness, or ultimate coating density. Magnetron DC sputtering of elemental boron is considered difficult, because the element is not electrically conductive and thus requires the far more inefficient method of RF or pulsed sputtering to frequently discharge the sputtering target. Similarly, plasma spray of elemental boron has been attempted on numerous occasions, but the high thermal stability of boron combined with the lack of electrical conductivity make the plasma stream very difficult to maintain and thus not commercially practical. Cathodic arc is another of the high throwing power industrial coating methods that does not perform well with elemental boron. Cathodic arc depends on making the feedstock of elemental boron the cathode of an anode-cathode arc discharge, and this requires electrical conductivity of the boron.

The methods of depositing boron may also be combined with the deposition of other coatings simultaneously as well as with the co-bombardment of energetic ions for enhancing the final density of the coating. Many other well-known combinations of deposition techniques exist which are compatible with the methods of depositing boron described herein.

Given that the boron precursor compound is electrically conductive, the following well known methods may be employed to deposit the coating. The advantage is that no special modification of the standard deposition technique is required to accommodate the electrically conductive boride.

1) Plasma spray (also flame spray or arc jet):

Electrically insulating elemental boron does not coat well due to charging in the arc chamber, but metal borides behave more like metals during coating. The required metal boride feedstock is a powder which can be produced in very finely divided form. Powder is the most commonly available form of most of the borides. This technique has been studied for the widest range of substrates. Plasma spray is defined here to encompass a wide variety of processes that utilize electric arc or plasma heating of a stream of material which is then directed towards a workpiece to form a coating. The stream typically consists of a material which is a gas at room temperature combined with a sprayable solid at room temperature, such as a fine powder. Alternatively, the stream may consist of a material which is a gas at room temperature combined with a partially vaporized material which is normally a solid at room temperature, such as one or more electrically conducting rods. The many variations of this process have a wide variety of specialized names including, but not limited to, plasma spray, flame spray, thermal spray, vacuum arc spray, electric arc spray, arc spray, vacuum plasma spray, cold spray, low pressure plasma spray (LPPS), plasma torch, thermal plasma torch, plasma jet, arc jet, arc torch, arc plasma, flame gun, D-gun, twin wire arc, plasma vapor deposition, and HVOF. The process may optionally include a selection of the gas species, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition.

2) Cathodic arc:

This method works only for electrically conducting feedstock, so boron is rarely deposited by this method at this time. A solid target is required. The cathode may consist of a

sintered boride cathode target, a melted boride powder, or a thick boride coating deposited onto a graphite or metal substrate by a technique such as plasma spray. Cathodic arc is defined here to encompass a wide variety of processes that utilize electric arc heating of a solid over sufficiently small areas to produce sufficient local heating to both vaporize the solid and cause the thermionic emission of large quantities of electrons. The resulting mixture of partially ionized vapor and uncharged particles impinges on a workpiece where a coating forms. The process may optionally include a selection of a carrier gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

3) Cathodic arc with mass filter:

material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as ion boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

4) Sputtering:

Elemental boron can be slowly sputtered using RF sputtering methods because it is an electrical insulator. However, the electrically conducting boride can be readily sputtered by the more efficient D.C. magnetron sputtering process or ion beam bombardment sputtering. Sputtering is defined here to encompass the class of coating processes that utilize ion bombardment of a source of material in order to dislodge and transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. The many variations of this process have a wide variety of specialized names including, but not limited to, D.C. magnetron sputtering, R.F. magnetron sputtering, AC magnetron sputtering, ion beam sputtering, D.C. sputtering, RF sputtering, or pulsed sputtering. The process may optionally include a selection of an ambient gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

5) Electric arc evaporation:

While elemental boron can be evaporated using electron beam or thermal boat evaporation methods, it is also possible to rapidly evaporate the metal boride using the heating

produced as electric current flows through the solid boride. Electric arc is defined here to encompass the class of evaporative coating processes that utilize an electric arc discharge between anode and cathode electrodes in order to heat and vaporize either the anode or cathode or both as a source of material in order to transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. Electrodes fabricated from an electrically conductive boride or boron-doped material can be utilized as an efficient source of boron vapor. The process may optionally include a selection of an ambient gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

6) Resistive evaporation:

The boride material has been pressed, sintered, crystallized, and plasma sprayed, as methods to create filaments and electrodes. Any of these methods may be employed to make resistance evaporation sources. Direct electrical heating is defined here to encompass the class of evaporative coating processes that utilize the resistive passage of electricity through an electrically conductive material in order to heat and vaporize the material in order to transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. An electrode fabricated from an electrically conductive boride or boron-doped material can be utilized as an efficient source of boron vapor. The process may optionally include a selection of an ambient gas species and its ambient

pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

7) Photon- or electron-induced evaporation:

Impingement of sufficiently energetic electrons or photons may easily be employed by traditional methods to create sufficient vapor for any of the instant applications. Photon-induced evaporation is defined here to encompass the class of evaporative coating processes that utilize photon-induced heating in order to heat and vaporize a material in order to transfer individual atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. Electron-induced evaporation is defined here to encompass the class of evaporative coating processes that utilize energetic electron beam-induced heating in order to heat and vaporize a material in order to transfer atoms or clusters of atoms to a separate workpiece where a coating of the transferred atoms or clusters of atoms is accumulated. An evaporative source fabricated from a boride or boron-doped material can be utilized as an efficient source of boron vapor. The process may optionally include a selection of an ambient gas species and its ambient pressure, a selection of the temperature of the workpiece during material deposition, and/or a selection of the bias voltage applied to the workpiece during material deposition. When the temperature of the workpiece is elevated above 500°C and preferably higher, the process may be referred to as boridizing, which includes the diffusion of boron atoms beneath the workpiece surface.

These deposition processes may also co-deposit other materials with the boron in order to further modify properties for enhanced materials. For example, boron carbide (B_4C) is also a poor electrical conductor because it is covalently bonded. It is normally deposited using chemical vapor deposition. The addition of boron carbide powder and optionally fullerene carbon powder to the metal boride powder in plasma spray can allow the deposition of a boron carbide-like coating onto materials.

All of these applications and deposition techniques depend on the existence of an electrically conductive metal boride that consists of and can be deposited as substantially pure boron.

Ultra-high boron atomic ratio materials have been demonstrated to produce substantially pure monoatomic boron and boron cluster vapor when sufficiently energized. Under proper growth conditions wherein temperature, pressure, atmosphere, and electromagnetic fields may be controlled, these vapors have been demonstrated to self-organize into various forms such as single and layered sheets, bundles of fibers, nanotubes of various kinds, spheres, and new crystalline forms such as B_{32} . These have been predicted to have desirable properties for applications in electronics, electro-optics, optics, nanofabrication, surface modification and alloying of metals and ceramics, and physio-chemical applications such as propulsion, energy storage, neutron attenuation, and alpha particle generation. Some of these materials have also demonstrated hydrophilic properties which are highly desirable for medical applications where a large neutron absorbing cross section is required.

These boron vapors are extremely reactive, demonstrating properties not evidenced in vapors derived from traditional boron -halide, -hydride, -carbide, -sulfide, -nitride, or -metal compounds. Early experiments have shown remarkable potential in wide areas of physical chemistry. By changing the background gas from inert to reactive, byproducts have been observed and analyzed, indicating that it is reasonable to expect new families of compounds in the carbides, hydrides, nitrides, halides, sulfides, and metals. Because of the novel physical and chemical properties of these vapors, it has also been possible to induce bonding of materials, such as tantalum and graphite, at temperatures well below what might be expected to be the temperature of what in this case would be TaC. Materials as dissimilar as zirconium oxide and molybdenum have been observed to bond in similar circumstances. The precursor material, when in the mixed vapor state, has been observed to adhere readily to Al, Al₂O₃, C, Si, SiO₂, W, Ta, Mo, steel, WC, Cu, aerogel, etc. The mechanism is believed to be some combination of physio-chemical boundary layering effects such that the boron vapor reacts with both surfaces to create the bond, in effect acting as a glue. Given the dissimilarity of materials so far tested, and the potential reactivity of boron, this would seem to indicate that novel compounds could be predicted for all materials but the noble gases, which simply facilitate the creation of new boron forms, which may each themselves have unique properties.

Alternatively, carbon fullerene vapors are combined with the above-mentioned boron vapors to form novel cluster and nanotube related structures. It is also predicted, that in the presence of sulfur, these boron and boron-carbon structures will take on properties conducive to the filling of the open volumes of the cluster and nanotube structures with different structures, for example nanotubes filled with spheres or solid material. Such materials would be electrically

conductive and would potentially have use as feedstock material for any of the processes listed above.

The invention further includes:

1. A method of creation of targets for sputtering, cathodic arc, electron beam, and laser ablation processing.
2. A method of lining or fabricating free-standing refractory crucibles to protect from chemical attack
3. A method of depositing the material on a removeable form for the creation of freestanding parts demonstrating the above-mentioned properties.
4. A method of making heating elements from these materials as coatings or freestanding parts.

Materials with boron ratios of 12 or greater may also be used for conductive coating purposes where the metal component volatilizes before or congruent with the boron fraction.

Examples of such materials may be found in different groups in the periodic table. The following list is intended to be exemplary, but not exhaustive. Group 2A: MgB_{12} , Mg_2B_{14} ; Group 3B: ScB_{12} , LaB_{66} , NdB_{66} , SmB_{66} , ThB_{66} , NpB_{12} , PuB_{12} , UB_{12} , AmB_{12} ; Group 4B: ZrB_{12} , HfB_{12} ; Group 5B: TaB_{12} ; and Group 6B: MoB_{12} , WB_{12} .

BRIEF SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a method for generating substantially pure boron which may be a useful source of coating material.

It is a further object of this invention to provide such a method for generating substantially pure boron such that the coating feedstock and the resultant coating are electrically conductive.

It is a further object of this invention to provide such a method for generating substantially pure boron such that extremely thick coatings can be obtained using well known coating technologies.

It is a further object of this invention to provide such a method for generating substantially pure boron such that the use of toxic chemicals may be avoided.

It is realized that the use of elemental boron as a feedstock in various well known coating technologies, such as cathodic arc, plasma spray, DC magnetron, electric arc, inductively heated evaporation, and electric current heated powder evaporation, does not perform reliably due to the lack of electrical conductivity and high thermal stability of elemental boron.

It is further realized that there exist metal boride compounds in which the companion metal represents less than 8 atomic percent of the compound.

It is further realized that said metal boride compounds are all electrically conductive.

It is further realized that when the companion metal does not readily vaporize, the metal remains present, permitting a gradual thermal decomposition through successive borides from a high boron-to-metal ratio towards the ratio of 4.

It is further realized that of the metal borides, only yttrium, holmium, erbium, thulium, terbium, gadolinium, and lutetium borides do not readily vaporize the metal component together with the boron.

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The phase diagram of yttrium and boron is shown in Figure 1. It shows that the higher boron-to-metal ratio borides decompose prior to melting. There exists a lower ratio boride that decomposes at a higher temperature in each case, thus indicating that there will be a successive loss of boron as a vapor with the next lower ratio boride as the decomposition product until YB_4 is reached. The phase diagram shows that YB_4 does not decompose in the solid state and is the most refractory of the several borides. Thus, it is the end product of the chain of decomposition. This interpretation of the phase diagram is confirmed experimentally by data presented in *The Handbook of High Temperature Compounds* (Kosalapova, 1990), pages 175-176, incorporated herein by reference. The table on these pages gives the measured vapor pressure of species resulting from thermal decomposition of most of the metal borides. It may be seen from the table that only yttrium, holmium, erbium, thulium, terbium, gadolinium, and lutetium borides decompose to only pure boron vapor instead of metal and boron vapor. It may also be seen that only the hexaborides and the higher atomic ratio borides of these metals decompose in this manner.

The log of the vapor pressure of boron is given in the table only at 1823°K (1550°C). When converted into millitorr units, the values for YB_6 , HoB_6 , and ErB_6 are 4.6, 34, and 56 millitorr. These values are typically quite temperature sensitive, increasing rapidly with greater temperature. These vapor pressure values are in the range suitable for use for physical vapor deposition and coatings.

The borides that have greater boron-to-metal ratios provide the greatest amount of boron vapor before the decomposition is halted at the tetraboride state. Thus, it is preferable to use

feedstock material that is as enriched as possible in the higher boron ratios and which has as little as possible of the lowest ratios, typically the diboride and tetraboride.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Other objects, features and advantages will occur to those skilled in the art from the following description of a preferred embodiment and the accompanying drawings in which:

FIG. 1 is a copy of the phase diagram of yttrium and boron taken from the ASM Metals Handbook, volume 1, page 556, incorporated herein by reference.

FIG. 2 is a copy of an EDAX measurement of the coating produced in EXAMPLE 5. The peak at the far left is due to boron coating. The other peaks are from the glass substrate.

EXAMPLE 1

YB₆₆ powder in the form of typically 50 to 75 micrometer particles has been used as the feedstock in an industrial plasma spray system utilizing argon gas as a carrier. The powder has been observed to spray easily and produce a characteristic granular deposit which can readily be built up to considerable thickness easily exceeding 3 mm. The deposit adheres readily to a wide variety of materials, including aluminum, steel, titanium, carbon, molybdenum, tungsten, tantalum, silicon, alumina, silica, zirconia, boron nitride, porcelain, and an aerogel foam. Good adhesion has been observed for all substrate materials tested. The resultant coating layer is extremely hard and difficult to break. In the case of a carbon substrate, for example, the graphite substrate will typically split or shatter prior to the debonding or failure of the coating. The

coating has been rapidly deposited over large surface areas and surfaces with complex shapes using well known plasma spray methods.

EXAMPLE 2

YB₆₆ has been plasma spray coated onto a tungsten coil filament for use as an electron emitter in an ion source. In addition, other ion source components, including the molybdenum arc chamber walls and graphite electron repeller, have been similarly coated in order to produce an ion source with enhanced boron emission as well as to minimize the output of contaminating atomic species. The tungsten coil filament has been heated to near its normal operating temperature when only the tungsten surface is exposed, and the filament has been observed to produce electrons capable of sustaining the arc discharge of the ion source. The coating was found to melt at the operating temperature of the filament, but the liquid coating did not alter the electron emission properties. The coated filament was found to enhance the boron output of the ion source, and the coating was not observed to detract from the normal filament lifetime, and tungsten contamination of the plasma was significantly diminished. If a boride is taken from the list in which the boron vaporizes preferentially before the metal, for example YB₆₆, then there is little or no metal component in the resultant ion beam according to a magnetic mass analysis of the beam.

EXAMPLE 3

A DC magnetron sputter target has been formed using buildup of a 1.5 mm thick coating of YB₆₆ using plasma spray. The sputter target transferred boron at a rate which was approximately 10 times greater than from RF sputtering. Sputter targets have been made by coating on a backing of graphite, copper and other materials.

EXAMPLE 4

A cathodic arc cathode has been formed in a few minutes by plasma spray of YB_{66} onto a graphite substrate. The coating was 3 mm thick. A cathodic arc system was operated with the said cathode at an arc current of nominally 50 Amperes in a background pressure of 10 millitorr of argon for 5 minutes. The output of the cathodic arc was directed towards a glass microscope slide target, and a grey, highly reflective boron-rich deposit was produced which was about 5 micrometers thick.

EXAMPLE 5

A high electric current of 75 Amperes has been drawn between two graphite electrodes connected by an excess of YB_{66} powder while in vacuum. The powder was observed to melt and begin emitting boron vapor, which could be used to coat a glass slide test sample. The thickness of powder separating the electrodes has been up to 2.5 cm, demonstrating the electrical conductivity of the boride. A high coating rate of over 0.003 inches per minute at a distance of 2 inches from the evaporation source was observed. FIG. 2 shows an EDAX analysis of the resultant coating material. EDAX is insensitive to light elements, such as boron, so the boron peak observed at the far left in the mass spectrum appears unnaturally small compared to the background elements from the glass slide substrate.

EXAMPLE 6

Nanostructures of boron have been fabricated in the form sheets, coiled nanotube-like tubular sheets, and wire-like filament structures. The structures have appeared following operation of a plasma chamber using a nitrogen + hydrogen mixture known as forming gas. The types of structures varied with collecting surface temperature, which was typically in the range of

800 to 1000 degrees centigrade. The materials were hydroscopic which could be reversed in vacuum. The observed structures could change form following this process.

Although specific features of the invention are shown in some drawings and not others, this is for convenience only and some features may be combined with any or all of the other features in accordance with the invention.

Other embodiments will occur to those skilled in the art and are within the following claims:

What is claimed is:

1. A method for depositing a coating substantially composed of the element boron or an isotope of the element boron comprising the steps of:

- i. Selecting a substrate for receiving said coating;
- ii. Selecting an electrically conductive boron-rich feedstock in which the initial ratio of boron to a companion element is 20 or greater for said coating;
- iii. Selecting a method for depositing said coating on said substrate from the group comprised of: plasma spray, cathodic arc, mass filtered cathodic arc, sputtering, electric arc, direct electrical heating, electron-induced evaporator, or photon-induced evaporation, and
- iv. Depositing said coating on said substrate.

2. The method of claim 1 in which said electrically conductive boron-rich feedstock is comprised of a compound of boron.

3. The method of claim 2 in which said companion elements of said electrically conductive boron-rich feedstock is one or more selected from the group comprised of elements from group 3B of the periodic table, including the rare earth elements, the actinides, and the lanthanides.

4. The method of claim 2 in which said companion elements of said electrically conductive boron-rich feedstock is one or more element selected from the group comprised of hydrogen, lithium, carbon, sodium, magnesium, nitrogen, and sulfur.
5. The method of claim 1 in which said electrically conductive boron-rich feedstock consists of a doped solid solution of said companion elements within boron.
6. The method of claim 5 in which said companion elements of said electrically conductive boron-rich feedstock consists of one or more element selected from the group comprised of the transition metals and Group 3B elements, including the rare earth elements, the actinides, and the lanthanides.
7. The method of claim 1 in which said substrate is temperature-controlled.
8. The method of claim 1 in which said substrate is voltage-controlled.
9. A method for depositing a coating substantially composed of the element boron or an isotope of the element boron comprising,
 - i. Selecting a substrate for receiving said coating;
 - ii. Selecting an electrically conductive boron-rich feedstock in which the initial ratio of boron to a companion element is 20 or greater;
 - iii. Selecting a method for depositing said coating on said substrate from the

group comprised of plasma spray, cathodic arc, mass filtered cathodic arc, sputtering, electric arc, direct electrical heating, electron-induced evaporation, or photon-induced evaporation;

- iv. Selecting a carrier gas compatible with said feedstock and said method for depositing said coating;
- v. Selecting the composition and pressure of gases in the environment of said substrate, and
- vi. Depositing said coating on said substrate.

10. The method of claim 9 in which said electrically conductive boron-rich feedstock consists of a compound of boron.

11. The method of claim 10 in which the companion element of said electrically conductive boron-rich feedstock is one or more element selected from the group comprised of elements from group 3B of the periodic table, including the rare earth elements, the actinides, and the lanthanides.

12. The method of claim 10 in which the companion element of said electrically conductive boron-rich feedstock is one or more element selected from the group comprised of hydrogen, lithium, sodium, magnesium, nitrogen, and sulfur.

13. The method of claim 9 in which said electrically conductive boron-rich feedstock consists of a doped solid solution of companion elements within boron.

14. The method of claim 13 in which said companion elements of said electrically conductive boron-rich feedstock is one or more element selected from the group comprised of the transition metals and Group 3B elements, including the rare earth elements, the actinides, and the lanthanides.

15. The method of claim 9 in which said carrier gas is one or more element selected from the group comprised Group 8 inert gases, nitrogen, oxygen, methane, sulfur hexafluoride, sulfur dioxide, hydrogen, silanes, halogens, and hydrogen halides.

16. The method of claim 9 in which said gases in the environment of said substrate substantially excludes oxygen or water vapor.

17. The method of claim 9 in which said gases in the environment of said substrate comprise a chemically reducing atmosphere.

18. The method of claim 9 in which said gases in the environment of said substrate consist of a partial vacuum.

19. The method of claim 9 in which said substrate is temperature-controlled.

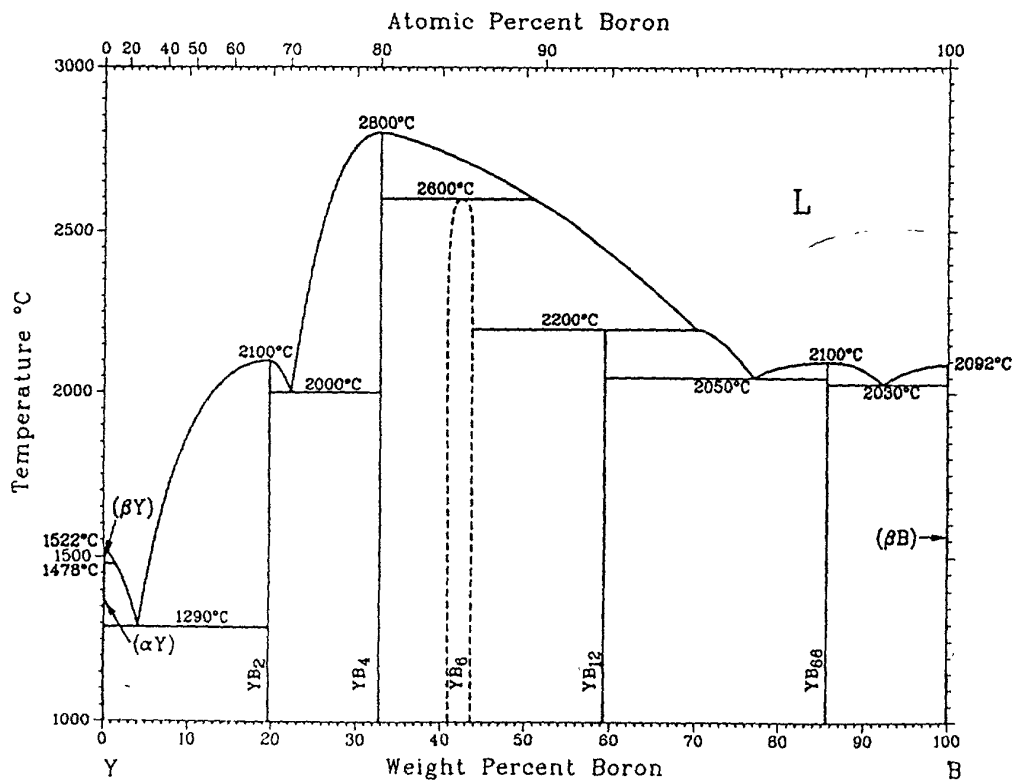
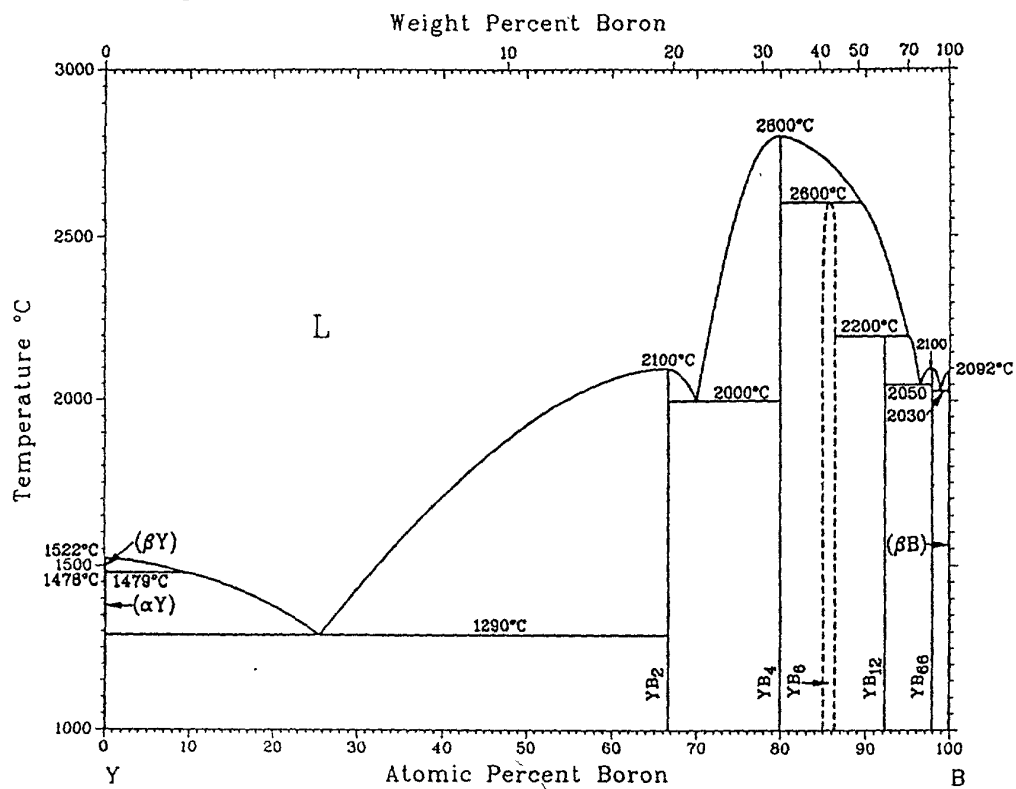
20. The method of claim 9 in which said substrate is voltage-controlled.

ABSTRACT OF THE DISCLOSURE

A method is disclosed for coating substantially pure boron or highly boron-rich borides in a controlled manner. Such a method of coating of boron has a variety of applications, including surface chemical and wear protection, neutron absorption, prevention of impurity emission from heated filaments and ion beams, elimination of metal dust from vacuum systems, boridizing, boron cluster emission, and reactive chemistry. Borides with a boron-to-metal ratio of 20 or more are known to exist and may be used as a feedstock for substantially pure boron coatings for deposition processes requiring feedstock electrical conductivity, and/or enhanced reactivity. While most metal borides coincidentally produce significant metal vapor as a by-product, certain borides of yttrium, holmium, erbium, thulium, terbium, gadolinium, and lutetium have been identified as capable of producing substantially pure boron vapor.



Y-B Phase Diagram



P.K. Liao and K.E. Spear, submitted to the APD Program.

FIG 1

Operator : JEOL
Client : All ISIS users
Job : Demonstration data SiLi detector
standard (8/4/99 11:46)

Counts

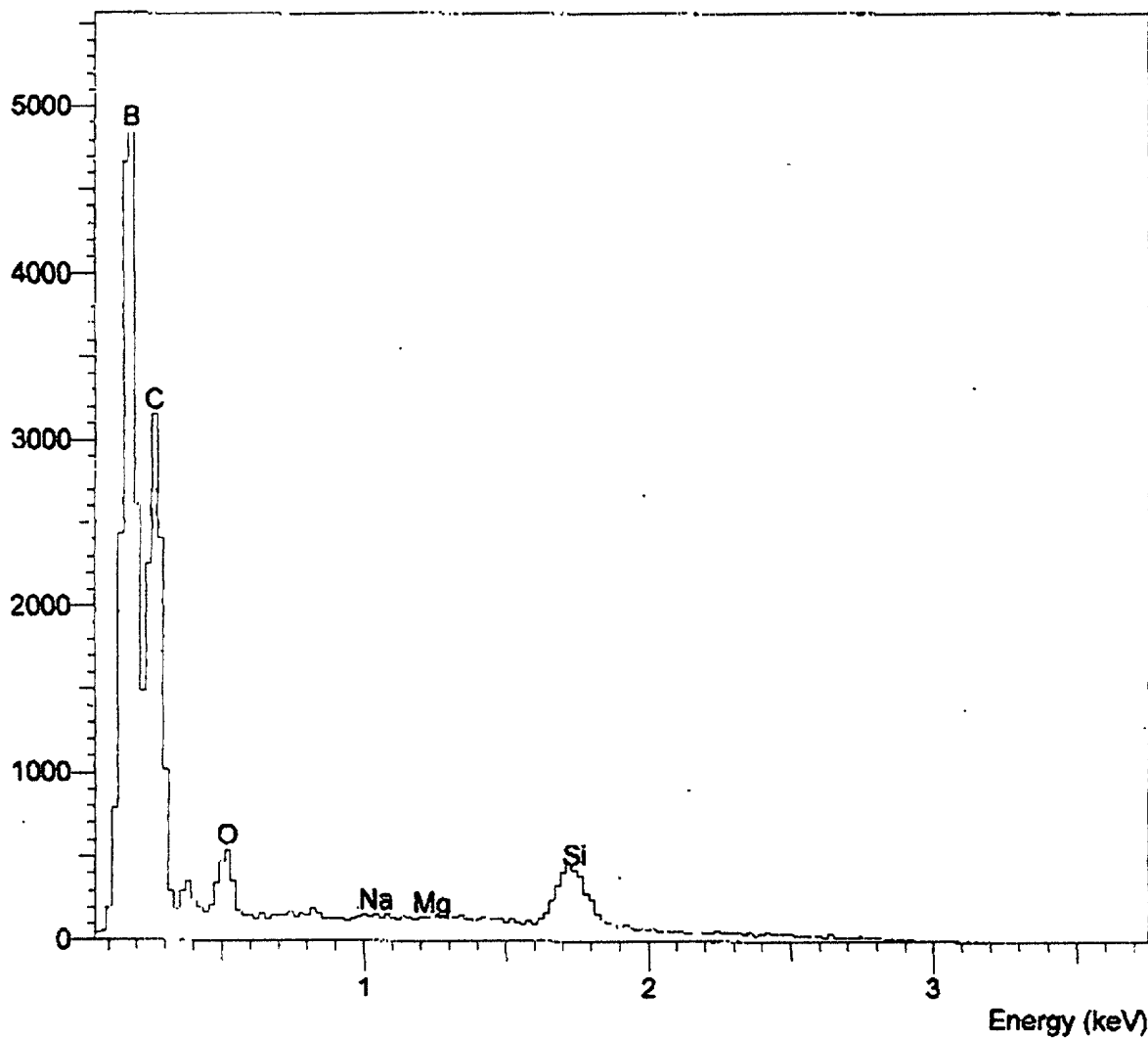


Fig 2